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Synthesis of Diels-Alder mono-adducts of methoxycarbonyl-1,4-benzoquinone

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Abstract: Diels-Alder reaction between 2-methoxycarbonyl-1,4-benzoquinone (I) and several dienes (1,3-butadiene, pipyrelene, isoprene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, spiro[4.1.2]hepta-1,3-diene and spiro[4.1.4]nona-1,3-diene) at various conditions were carried out. The stereochemistry of the mono-adducts were determined through ^{1}HNMR spectroscopy and photochemical reactions. The reactions almost occurred at the substituted enthene linkage of the quinone. There mono-adducts were prepared to serve as Michael acceptor for the consecutive work.
Keywords: 2-Methoxycarbonyl-1,4-benzoquinone, Diels-Alder reaction, cyclopentadiene, piperylene, 1,3-butadiene, 2,3-dimethylbutadiene, isoprene.

Introduction

A Diels-Alder reaction between an unsymmetrical 1,4-benzoquinone (I) and an unsymmetrical diene (II) can in principle give rise to four structurally distinct adducts having cis-ring junctions (figure 1). Factors controlling the 'side of addition' to give (III) or (IV) or alternatively (V) or (VI) have already been established.[1]It has been reported[2]that an unsymmetrically substituted 1,4-benzoquinone may undergo the Diels-Alder reaction at either of the ethene linkages, the nature of the substituents being the determining factor.

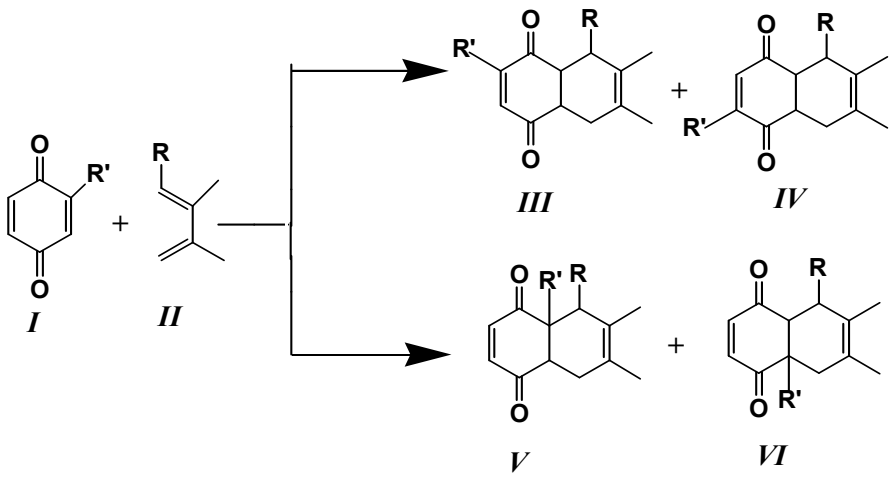


Figure 1

In Diels-Alder reactions of dienes with unsymmetrical 1,4-benzoquinones, the electron- withdrawing groups will activate the ethene linkage of the quinone to which they are attached, whilst electron-releasing groups will deactivate it. Ansell and co-workers[1]have shown that in any Diels-Alder reaction between a diene and a 1,4-benzoquinone, to decide to which ethene linkage of the quinone the diene will add, three factors must be considered:

(i) The electronic nature of the quinone substituents so that the more electron-deficient ethene linkage may be decided;

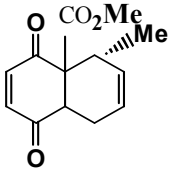
(ii) The number and size of the substituents that would be expected, on electronic grounds, to be angular in the products;

(iii) The size of the substituents on the 2,3-positions of the diene, and the non-bonded interactions with the quinone substituents in possible transition states.

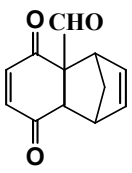
They also suggested that there is steric opposition to the formation of adducts with angular groups. A group in an angular position will be more compressed than it would be in a non-angular position or in the parent 1,4-benzoquinone.[2]Ansell and co-workers[1]have investigated extensively the reactions of mono-, di-, tri-, and tetrasubstituted-1,4-benzoquinones with 1,3-butadiene and 2,3-dimethylbutadiene; from the results obtained, they concluded that a quinone double bond to which CN, COMe, CO_2Me, or CF_3 is attached is activated as a dienophile, whereas attachment of MeO, Cl, F, etc. causes deactivation. Finally, on the basis of their results, they gave the following order of activating effects of groups on the Diels-Alder reactivity of a quinone double bond:

CN>COMe>CO_2Me>CF_3>H>F?>Cl>Me,
OAc>NMePh, MeO, SMe.

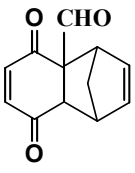
Goldsmith et al.[3]reported that the Diels-Alder reaction between piperylene and methoxycarbonyl-1,4-benzoquinone yielded the "ortho"product (VII) exclusively and quantitatively. Addition of cyclopentadiene to 1,4-benzoquinone occurs much more rapidly than addition of butadiene probably because in cyclopentadiene the double bonds are rigidly cisoid, and in principle can give both the endo- and exo –adducts. Usually, the endo – adduct is obtained, and its stereochemistry has been confirmed by photocyclization to the 'box compound'. Al-Sheibani[6]reported the reaction of formyl-1,4-benzoquinone with one equivalent of cyclopentadiene at room temperature; an 8:1 mixture of endo (VIII) and exo (IX) was obtained. Brown[4] has carried out reactions between acetyl-, propionyl-, isobutyroyl-, phenylacetyl-1,4-benzoquinones (X) and cyclopentadiene at room temperature and reported that all of them afforded mixtures of two adducts of type (XI, a-d), and only in the case of R=CH_2Ph (XI, d) was the pure major mono-adduct obtained. Coville[5] reported the reaction of methoxycarbonyl-1,4-benzoquinone (X, e) with cyclopentadiene, isolated and characterized (XII. e) as the major component. Pure endo adducts of type (XIV; a,b) have been obtained from the addition of cyclopentadiene to pivaloyl- and benzoyl-1,4-benzoquinone (XIII; a,b) at room temperature; steric (R=Bu^t) and electronic (R=Ph) effects probably control these additions.[5,]



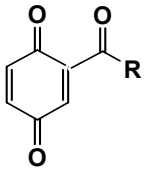
VII



VIII

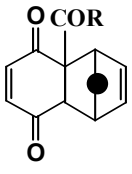


IX



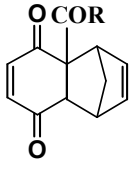
X

a. R , Me **d. R , CH_2Ph**
b. R , Et **e. R , OMe**
c. R , Pr^i



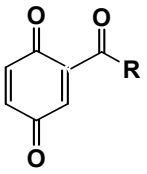
XI

a. R , Me **c. R , Pr^i**
b. R , Et **d. R , CH_2Ph**



XII

d. R , CH_2Ph
e. R , OMe



XIII

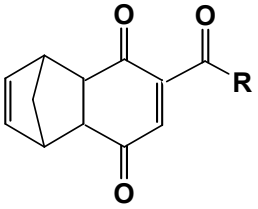
a. R , Bu^t
b. R , Ph

[1]Trifluoromethyl-1,4-benzoquinone reacts with cyclopentadiene at room temperature with or without solvent and gives a 4:1 mixture of endo (XVI) and endo (XVII) adducts, respectively.[6,7]Cyano-1,4-benzoquinone gives endo (XVIII) mono-adduct with one equivalent of cyclopentadiene in benzene at room temperature, in high yield after crystallization (XIX).[15]Refluxing of this adduct in benzene for 3 hours resulted in the formation of a second isomer (XX).

Addition of cyclopentadiene to a variety of simple alkyl-, aryl-, alkoxy-, alkylthio-, and arylthio-1,4-benzoquinones usually occurs readily[8-11] and almost without exception the products are endo-mono-adducts.[5] Reactions of a number of alkyl-1,4-benzoquinones with cyclopentadiene were reported[5,12] and all of the results indicate that the addition occurred at the unsubstituted side, and only mono-adducts could be obtained.

Experimental

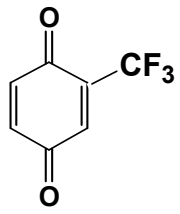
Nuclear magnetic resonance (n.m.r.) spectra were recorded with Perkin-Elmer R12B (60 MHz), R32 (90 MHz) and R34 (220 MHz) spectrometers, respectively. Tetramethylsilane (TMS) was used as an internal standard and coupling constants (J) are expressed in Hz. Infrared spectra were measured using a Pye Unicam SP3-200 Spectrophotometer. Low resolution Electron Impact (EI) mass spectra were recorded on A.E.I. MS30 and Kratos MS25 instruments; mass measurements (M.M.) were made on the former, and Chemical Ionization (CI) spectra were recorded on the latter using ammonia as the reagent gas. Sublimation and bulb-to-bulb distillation temperature are those of the Buchi Oven (heating bath). All solvents, liquid reagent and starting material were distilled prior to use. Irradiation with visible light was carried out at 15 °C, using tungsten-filament lamps. Analytical and preparative TLC were carried out with Merck silica gel plates (5×10 cm×0.25 mm and 10×20 cm×0.25 mm), type $60F_{254}$.



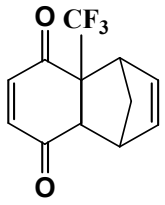
XIV

a. R, Bu^t

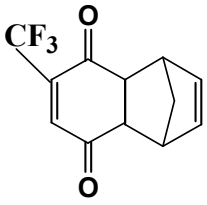
b. R, Ph



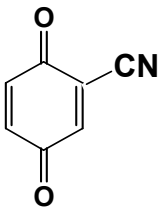
XV



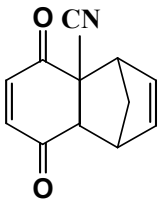
XVI



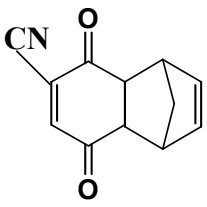
XVII



XVIII



XIX



XX

1.Preparation of 4a-methoxycarbonyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

a). At atmospheric pressure

To a stirred solution of 2-methoxycarbonyl-1,4-benzoquinone (332 mg, 2 mmol) in benzene (3 mL) at 0°C, trifluoroacetic acid (ca. 0.1 mL) was added. Butadine gas was passed into the mixture until the initial orange-red colour faded to pale yellow (ca. 3 min.). The mixture was left at 0°C for 0.5 hour. Removal of the solvent and excess of butadiene first at 10°C/20 mmHg, then at 50°C/20 mmHg and finally at 0.1 mmHg gave a pale yellow sticky oil (427 mg, 97%). Sublimation at 130°C/0.3 mmHg gave a pale yellow soft crystalline compound which hardened on standing (352 mg, 80%), m.p. 47-51°C (lit.[13]50-52). (Found: C, 64.6; H, 5.4. Calc. for $C_{12}H_{12}O_4$: C, 65.5 ; H, 5.45%). It had δ (5%, $CDCl_3$, 90 MHz) 6.63 (s, H-2 + H-3), 5.64 (m, collapsed to a singlet on irradiation at δ 2.60, 2.30, H-6 + H-7), 3.74 (s, CO_2Me), 3.64 (t, J=6, collapsed to a singlet on irradiation at δ 2.55, H-8a), 2.15-2.70 (m, sharpened on irradiation at δ 5.64, 3.64, 2× H-5 + 2×H-8) ; δ (5%, C_6D_6, 90 MHz) 5.99 (s, H-2 + H-3), 5.35 (bs, sharpenedt on irradiation at δ 2.35, 2.20, 1.85 H-6 + H-7), 3.36 (t, J=6, splitted to a dd, J_{-1}=6, J_{-2}=4, on irradiation at δ 2.35, and to a dd, J_{-1}=7, J_{-2}=2, on irradiation at δ 2.20,H-8a), 3.25 (s, CO_2Me), 1.70-2.50 (m, 2× H-5 + 2×H-8) ; ν ˉ (cm^{-1})(CH_2Cl_2) 3040 w, 2965 w, 1740 s, 1690 s, 1610 w, 1240 s; m/z (E.I.) 220 ($M^{\cdot+}$, 3), 188 [(M-MeOH) $^{\cdot+}$, 17], 161[(M-CO_2Me) $^+$, 100], 160[(188-CO) $^{\cdot+}$, 82], 133 [(161-CO) $^+$, 27], 105[(133-CO) $^+$, 43], 82[(OC. CH=CH.CO) $^+$, 60], 77 (77), 54[(H_2C = CH.CH=CH_2)$^+$, 59]; (C.I.) 238 [(M+18)$^+$, 76], 221 [(M+H)$^+$, 36]. Crystallization of (427 mg) of another batch of the crude product (before sublimation) from hot pentane (twice) afforded a white-yellow crystalline compound (284 mg, 56%), m.p. 54-56 °C (lit.[13]50-52 °C).

b) In a sealed tube

2-Methoxycarbonyl-1,4-benzoquinone (498 mg, 3 mmol) was dissolved in benzene (3 mL) and a few drops of trifluoroacetic acid added. The solution was transferred to a drawn-out test tube, and cooled in solid carbon dioxide. Butadiene gas was passed in until liquid butadiene (ca. 2mL) had condensed on the solid solution. The tube was partially evacuated, sealed and left at room temperature for 2 hours. The initial orange colour changed to pale yellow. The tube was cooled in solid carbon dioxide, opened, and warmed up to room temperature to allow the excess of butadiene to evaporate. Removal of the solvent first at 20°C/20 mmHg, then at 50°C/20 mmHg and finally at 0.1 mmHg gave a yellow oil which slowly solidified on standing at room temperature (550 mg, 83%). Its NMR spectrum ((5%, $CDCl_3$, 90 MHz) was identical with the spectrum described in (a).

2.4a β-Methoxycarbonyl-5α-methyl-4a,5,8,8a β-tetrahydro-1,4-naphthoquinone

(a). Trans-piperylene (82 mg) was added to a solution of 2-methoxycarbonyl-1,4-benzoquinone (200 mg, 1.205 mmol) in benzene (3 mL), and the mixture was left at room temperature for 2 hours. The initial deep yellow colour faded to pale yellow. Removal of the solvent gave a yellow oil (275 mg, 98%). Sublimation at 118°C/0.05 mmHg gave a yellow oil (230 mg, 82%). (Found: C, 65.7; H, 5.8. Calc. for $C_{13}H_{14}O_4$: C, 66.7 ; H, 5.98%). NMR spectroscopy had shown that the sublimate was a mixture of cis and trans isomers (3:1), respectively. The cis isomer had δ (5%, $CDCl_3$, 90 MHz) 6.19 (s, H-2 + H-3), 5.60 (m, H-6 + H-7), 3.78 (s, H-8a + CO_2Me), 3.0(m,H-5), 2.68(dm, J_{-1}=18, H-8α or H-8β), 2.13 (dm, J_{-1}=18, H-8β or H-8α), 1.02 (d, J=7.4 collapsed to a singlet on irradiation at δ3.0, 5-Me); the trans isomer had δ 3.63 (s, CO_2Me), 1.05 (d, J=7, Me); δ (4%, C_6D_6, 90 MHz), cis isomer: 6.13 (s, H-2 + H-3), 5.44 (m, H-6 + H-7), 3.54 (dd, J_{-1}=7.4, J_{-2}=4.5, collapsed to a triplet, J=4, on irradiation at δ 2.50, and to a doublet, J=6, on irradiation at δ 1.90,H-8a), 3.34 (s, CO_2Me), 3.08 (m, sharpened on irradiation at δ 4.56, 0.88, H-5), 2.63 (dm, J_{-1}=19, J_{-2}=2.4, sharpened on irradiation at δ 5.44, 3.50, H-8α or H-8β), 1.88 (ddd, with fine structure, J_{-1}=19, on irradiation at δ 3.50, and to a dd, J_{-1}=19, J_{-2}=7, on irradiation at δ 2.90, H- 8β, or H-8α), 0.88 (d, J=8, collapsed to a singlet on irradiation at δ 2.90, Me); trans isomer: δ 0.90 (d, J=8, Me); ν ˉ (cm^{-1})(neat) 3030 w, 2960 w, 1745 s, 1675 s, 1605 w, 1255 s; m/z (M.M.) 234.0892($M^{\cdot+}$, 3.6); (C.I.) 252 [(M+18)$^+$, 97], 235 [(M+H)$^+$, 100]; (E.I.) 234 ($M^{\cdot+}$, 5), 202[(M-MeOH) $^{\cdot+}$, 52], 175[(M-CO_2Me) $^+$, 100], 174[(204-CO) $^{\cdot+}$, 78], 160 [(175-Me) $^+$, 19], 159[(174-Me) $^+$, 17], 131[(160-CHO) $^+$ or (159-CO)$^+$, 31], 105[(131-C_2H_2)$^+$, 18], 91 (53), 77 (43).

(b) 2-Methoxycarbonyl-1,4-benzoquinone (83 mg, 0.5 mmol) was dissolved in benzene (3 mL), trifluoroacetic acid (3 drops), and trans-piperylene (34 mg) were added. The mixture was refluxed for 1 hour, then cooled to room temperature. Removal of the solvent gave a pale yellow oil (115 mg, 98%). Sublimation at 120°C/0.1 mmHg gave a pale yellow oil (109 mg, 93%), spectra and analyses of which were almost identical with those of cis-isomer described in **(a)**. Therefore, although the addition reaction[13,3]gives the cis-mono-adduct, sublimation causes isomerisation giving a 3:1 cis-trans mixture.

3.4a-Methoxycarbonyl-7-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

Trifluoroacetic acid (0.1 mL) was added to a solution of 2-methoxycarbonyl-1,4-benzoquinone (144 mg, 0.867 mmol) in methylene chloride (3 mL) at 0 °C. Isoprene (59 mg, 1 equ.) was then added at 0 °C, and the mixture was maintained at this temperature for 1 hour.Removal of the solvent gave a pale dark green mobile oil (166.5 mg, 82%). Sublimation at 125°C/0.3 mmHg gave a pale yellow oil (118.5 mg, 58%). (Found: C, 66.2; H, 6.2. Calc. for $C_{13}H_{14}O_4$: C, 66.7 ; H, 6.0%). The major isomer (90%) had δ (8%, $CDCl_3$, 220 MHz) 6.67 (s, H-2 + H-3), 5.37 (m, H-6), 3.75 (s, CO_2Me), 3.63 (t, J=4, H-8a),2.65(dm, J_{-1}=18, H-5α or H-5β), 2.45(dm, J_{-1}=18, H-5β or H-5α), 2.35 (dm, J=19, collapsed to a bm on irradiation at δ2.06, and sharpened on irradiation at δ3.63, H-8β or H-8α), 2.06 (dm, J=19, collapsed to a bm on irradiation at δ2.35, and sharpened on irradiation at δ3.63, H-8α or H-8β), 1.65 (s, 7-Me). Absorptions at δ1.68 is due to the methyl of the minor isomer (10%). δ (5%, C_6D_6, 220 MHz), 6.06 (AB-q, J=9.8, H-2 + H-3), 5.14 (sharpened on irradiation at δ 2.40, H-6), 3.44 (t, J=6.8, + H-7), 3.54 (collapsed to a doublet, J=5, on irradiation at δ 2.24, and 1.84, H-8a), 3.27 (s, CO_2Me), 2.40 (AB-q, J=17, sharpened on irradiation at δ 5.14, 2×H-5), 2.24 (dm, J_{-1}=18, sharpened as a part of an AB-q with δ 1.84, on irradiation at δ 3.44, H-8α or H-8β), 1.84 (dm, J_{-1}=18, sharpened as a part of an AB-q with δ 2.24, on irradiation at δ 3.44, H- 8β, or H-8α), 1.41(s, 7-Me); Absorption at δ 6.04 (AB-q), and δ 1.34 (s) are due to the minor isomer; ν $^-$ (cm^{-1})(film) 3035 w, 2950 w, 1735 s, 1685 s, 1605 w, 1235 s; m/z (E.I.) 234 ($M^{\cdot+}$, 7), 215 [(M-Me) $^+$, 13], 202[(M-MeOH) $^{\cdot+}$, 15], 175[(M-CO_2Me) $^+$, 56], 174 [(M-HCO_2Me) $^+$, 61], 160[(175-Me) $^+$, 17], 159 [(174-Me) $^+$, 17], 147[(175-CO) $^+$, 27], 119[(147-CO) $^+$, 51], 107[(75-C_5H_8)$^+$, 32], 93 [(119-C_2H_2)$^+$, 46], 91 (89), 69 (96), 41 (100); (C.I.) 252 [(M+18)$^+$, 20], 235 [(M+H)$^+$, 79], 175 [(M-CO_2Me) $^{\cdot+}$, 20], 174 [(M-HCO_2Me) $^+$, 21],147[(175-CO) $^+$, 12], 119[(147-CO) $^{\cdot+}$, 11], 19 (100). The minor isomer (10%) is probably 4a-methoxycarbonyl-6-methyl-4a,5,8,8a-tetrahydro- 6.22,

4.Endo-cis-4a-methoxycarbonyl-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

(a) With trifluoroacetic acid

Trifluoroacetic acid (0.25 mL) was added to a stirred solution of 2-methoxycarbonyl-1,4-benzoquinone (500 mg, 3.01 mmol) in methylene chloride (10 mL) at -35 °C. The mixture was then cooled to -60 °C and freshly prepared cyclopentadiene (200 mg, 3.03 mmol) was then added. The reaction mixture was maintained at -70 °C for 1 hour, then warmed to room temperature. Removal of the solvent first at 20°C/20 mmHg then at 40°C/0.1 mmHg gave a yellow orange mobile oil (685mg, 98%). It had δ (6%, $CDCl_3$, 90 MHz) 6.67 (s, H-2 + H-3), 6.22 (m, sharpened on irradiation at δ 6.20, H-6 + H-7), 3.85 (s, partially buried under the CO_2Me absorption, sharpened on irradiation at δ 6.22, H-8 or H-5), 3.75 (s, CO_2Me), 3.49(bs ,H-5 or H-8), 3.45(d, J=4, partially overlapped with δ 3.49, H-8a), 1.70 (bs, 2×H-9); δ (6%, C_6D_6, 90 MHz) 6.10 (s, H-2 + H-3), 5.79 (m, sharpened on irradiation at δ 3.80, H-6 + H-7), 3.80 (m, sharpened on irradiation at δ 5.79, 1.40, H-5 or H-8), 3.17-3.37 (m, buried under r the CO_2Me absorption, H-8 or H-5), 3.21 (s, CO_2Me), 3.12 (d, J=4, H-8a), 1.40 (m, sharpened to an AB-q, J=10, on irradiation at δ 3.80, 2× H-9), as the major component (66%). The minor component had δ (6%, $CDCl_3$, 90 MHz) 7.45-8.0 (b, OH), 6.88 (AB-q, J=9, 2×H, aromatic), 5.70-6.05 (m, 2×H, olefinic), 4.25-4.55 (m, H), 3.99 (s, CO_2Me), 1.95-3.35 (m, 3×H); δ (5%, C_6D_6, 90 MHz) 6.79 (s, 2×H, aromatic), 5.40-5.75 (m, 2×H, olefinic), 3.85-4.10 (m, H), 1.80-2.57 (m, 3×H); which suggests that the minor component produced on warming up of the crude product may be (XXXI); ν $^-$ (cm^{-1})(film) 3010 w, 2960 w, 1743 s, 1670 s, 1615 w, 1220 s; m/z (E.I.) 233 [(M+1)$^+$, 2], 232 [(M)$^{\cdot+}$, 12], 200 [(M-MeOH) $^{\cdot+}$, 31], 173[(M-CO_2Me) $^+$, 11], 172[(200-CO) $^{\cdot+}$, 9], 167 [(M+1-C_5H_6)$^{\cdot+}$, 13], 136 [(167-MeO)$^+$, 15], 135 [(167-MeOH) $^{\cdot+}$, 13], 107[(135-CO) $^{\cdot+}$ or (172- C_5H_6)$^{\cdot+}$, 6], 66 (C_5H_6, 100)$^+$; (C.I.) 250 [(M+18)$^+$, 17], 233 [(M+1)$^+$, 90], 184 [(250- C_5H_6)$^+$, 66], 169 (100).

Crystallization from cyclohexane gave an oil which solidified on scratching and after washing with pentane afforded the mono-adduct (350 mg, 50%), m.p. 49-53 °C (lit.[13]55-57.5 °C). The crystalline compound (100 mg) was sublimed, giving: (i) At 105°C/0.1 mmHg a yellow sticky oil (20 mg), mostly (NMR) endo-mono-adduct. (ii) At 123-125°C/0.1 mmHg , a pale yellow oil (20 mg), almost pure (NMR) endo-mono-adduct.

(b). Without trifluoroacetic acid

Cyclopentadiene (40 mg, 1 equ.) was added to 2-methoxycarbonyl-1,4-benzoquinone (100 mg, 0.602 mmol) in benzene (10 mL) at room temperature; the initial orange colour faded to pale yellow. The mixture was left at room temperature for 12 hours. Removal of the solvent at 20 °C/20 mmHg gave a pale yellow sticky oil (130 mg, 93%). It had δ (10%, $CDCl_3$, 60 MHz) 6.90 (bs, H-2+H-3, exo), 6.64 (s, H-2+H-3, endo), 5.96-6.40 (m, H-6+H-7 of endo, H-6+H-7 of exo), 3.16-4.0 (m, buried under the absorptions of CO_2Me groups of endo and exo, H-5+H-8+H-8a of exo, +H-5+H-8+H-8a of endo), 3.85 (s, CO_2Me of exo), 3.74 (s, CO_2Me, endo), 1.65 (bs, 2×H-9, endo), 1.50 (m, 2×H-9, exo); ν $^-$ (cm^{-1})(film) 3010 w, 2960 m, 1745 s, 1675 s, 1615 w, 1240 s; m/z (E.I.) 233 [(M+1)$^+$, 3], 232 [(M)$^{\cdot+}$, 20], 200 [(M-MeOH) $^{\cdot+}$, 16],

172[(200-CO) $^{\cdot+}$, 14], 167 [(M+1-C_5H_6)$^{\cdot+}$, 28], 136 [(167-MeO)$^+$, 8], 135 [(167-MeOH) $^{\cdot+}$, 13], 107[(135-CO) $^{\cdot+}$,6], 66 ($C_5H_6^+$, 100). From the NMR spectrum it was concluded that the adduct was a 76:24 mixture of endo and exo-isomers, respectively.

5.Treatment of 2-methoxycarbonyl-1,4-benzoquinone with spiro[4.1.2]hepta-1,3-diene

Spiro[4.1.2]hepta-1,3-diene (92 mg, 1.equ.) (the spiro-compound was a 2:1 mixture with ethylene bromide; 260 mg of the mixture was used) was added to a solution of 2-methoxycarbonyl-1,4-benzoquinone (166 mg, 1 mmol) in benzene (5 mL) at room temperature and left for 64 hours. Removal of the solvent gave a brown oil. NMR spectroscopy showed that the product was a mixture of ethylene bromide and two mono-adducts, addition of spiro-compound on substituted side (B) and unsubstituted side (A), respectively.

It had δ (7%, $CDCl_3$, 60 MHz) 6.86 (s, H-3, A), 6.66 (s, H-2+H-3, B), 6.24 (m, H-6+H-7, A, +H-6+H-7, B), 3.87 (s, CO_2Me, B), 3.77 (s, CO_2Me, A), 3.67 (s, $BrCH_2$ CH_2Br), 3.44 (m, H-8a+H-5+H-8,B), 2.94 (m, H-4a+H-5+H-8+H-8a, A), 0.58 (s, 2×H-10+2×H-11, B). Integration showed that the mono-adducts (A) and (B) were in a 1:1 ratio. In order to remove ethylene bromide, the mixture was dissolved in freshly distilled carbon tetrachloride. Removal of the carbon tetrachloride and ethylene bromide gave an oil. This was repeated three times. The NMR spectrum then showed almost identical resonances to those described above, except that the absorption due to ethylene dibromide had been removed.

The reaction was repeated at 80 °C in benzene, at 130 °C in chlorobenzene, with trifluoroacetic acid in benzene at room termperature; NMR spectra showed almost the same results except at 130 °C in chlorobenzene which resulted in a mixture with the ratio of 2:1 or isomers A and B, respectively.

6. Preparation of a cage compound from the addition of 2-methoxycarbonyl-1,4-benzoquinone with spiro[4.1.2]hepta-1,3-diene

A mixture (50 mg) of the two mono-adducts from the addition of spiro[4.1.2]hepta-1,3-diene to the substituted and unsubstituted sides of 2-methoxycarbonyl-1,4-benzoquinone was dissolved in d_6-benzene (0.5 mL) and placed in an NMR sample tube, the mixture was irradiated with tungsten filament light at 20 °C and the progress of the reaction was monitored by NMR spectroscopy. Rapid photocyclization took place, showing that both mono-adducts were endo-isomers. The irradiation was continued for 17 hours, the solution then had δ (10%, $CDCl_3$, 90 MHz) 3.86 (s, CO_2Me, A), 3.83 (s, CO_2Me, B), 2.02-3.62 (m, 14×H, A+B), 0.79 (s, 2×H-12+2×H-13,B), 0.76 (s, 2×H-12+2×H-13,A); δ (10%, C_6D_6, 90 MHz) 3.47 (s, CO_2Me, A), 3.45 (s, CO_2Me, B), 1.40-3.40 (m, 14×H, A+B), 0.24 (s, 2×H-12+2×H-13,A+2×H-12+2×H-13,B); m/z (E.I.) 259 [(M+1)$^+$, 34], 258 [(M)$^+$, 44], 230 [(258-CO) $^{\cdot+}$, 20], 227[(M-MeO) $^+$, 17], 226 [(M-MeOH) $^{\cdot+}$, 14], 199[(M-CO_2Me) $^+$, 13], 198 [(M-HCO_2Me)$^{\cdot+}$, 20], 171[(199-CO)$^+$, 22], 170 [(198-CO) $^{\cdot+}$, 23], 115[(143-CO) $^+$,48], 92 [(C_7H_8)$^+$, 67], 91 [(92-H)$^{\cdot+}$, 100], 65[(91-C_2H_2)$^{\cdot+}$, 25].

7-Treatment of 2-methoxycarbonyl-1,4-benzoquinone with spiro[4.1.4]nona-1,3-diene

Spiro[4.1.4]hepta-1,3-diene (60 mg) (120 mg of its 1:1 mixture with 1,4-dibromobutane) was added to a solution of 2-methoxycarbonyl-1,4-benzoquinone (83 mg, 0.5 mmol) in methylene chloride (3 mL) at 0 °C and left for 4 hours. Removal of the solvent gave a yellow-brown sticky oil (220.6 mg). NMR spectroscopy showed that the product consisted of two mono-adducts (addition of the spiro-compound on substituted side of the quinone, B, and on the unsubstituted side ,A) in a ratio of 62:38, A to B, respectively.

It had δ (8%, $CDCl_3$, 60 MHz) 6.76 (s, H-3, A), 6.56 (bs, H-2+H-3, B), 6.0 (m, H-6+H-7, A, +H-6+H-7, B), 0.8-4.0 (m, H-4a+H-5+H-8a+2×H-10+2×H-11, 2×H-12+2×H-13,A+H-5+H-8+H-8a+2×H-10+2×H-11+2×H-12+2×H-13, B), 3.84 (s, CO_2Me, A), 3.71 (s, CO_2Me, B).

The reaction was repeated but with refluxing for 4 hours. NMR showed that the product was a mixture in which a particular adduct could not be identified. The reaction was repeated at room temperature. The same results as in those at the refluxing were obtained.

Discussion

The ultimate objective of this work was to prepare some mono-adducts between 2-methoxycarbonyl-1,4-benzoquinone (I) and a few dienes in order to use them as Michael acceptor compounds in other purposes. Addition of butadiene to 2-methoxycarbonyl-1,4-benzoquinone (I) in the presence of catalytic amount of trifluoroacetic acid (TFA) in benzene at 0 °C and at room temperature gave a pale yellow crystalline compound; the presence of TFA not only speede up the reaction previously described in the absence of catalyst by Akpuaka[13], but also caused almost exclusive regioselectivity to yield isomer (XXI). Ansell et al.[25]had reported that isomer (XXII) resulted from the uncatalysed addition of diene to the quinone. Ansell et al.[1] recorded a m.p. of 73-75 °C for the trans-isomer of (XXI); the cis-isomer was described as an oil whereas the m.p. found by the author is 47-51°C, and that by Akpuaka[13], is 50-52 °C, indicating the formation of the cis-isomer.

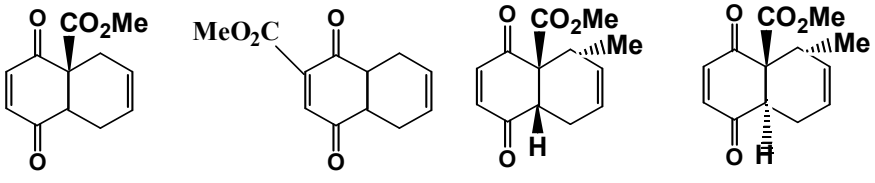
Trans-piperylene reacted with 2-methoxycarbonyl-1,4-benzoquinone in the presence of a catalytic amount of TFA to give exclusively the cis-isomer (XXIII), but sublimation of this adduct at 118°/0.05 mmHg afforded a 3:1 mixture of cis- and trans-isomers (XXIII) and (XXIV), respectively, the evidence for this being the appearance of two methoxycarbonyl resonances at δ 3.63 and 3.78 and two 5a methyl absorptions at δ 1.02 (d, J=7.4 Hz) and 1.05 (d, J=7 Hz). Formation of (XXIII)is controlled by the electron-withdrawing effect of the methoxycarbonyl group, with electrostatic effects predominating over steric ones. No sign of formation of isomers such as (XXV) or (XXVI) was observed. Akpuaka[13], and Goldsmith et al.[3] independently reported the formation of (XXIII) in a much longer reaction time without using TFA.

Isoprene reacted with 2-methoxycarbonyl-1,4-benzoquinone in methylene chloride in the presence of a catalytic amount of TFA and gave a 9:1 mixture of (139) and, probably (XXVIII) after sublimation of the mixture at 125 °C/0.3 mmHg. Separation was unsuccessful. The main features of the ^{1}HNMR spectrum of the sublimate in d-chloroform are: δ 1.65 [s, 7-Me, (XXVII)], and 1.68 [s, as a shoulder on δ 1.65, 6-Me, (XXVIII)]. The formation of (XXVIII) is surprising as using TFA increases the regioselectivity, although the control is normally less for isoprene than for trans-piperylene.

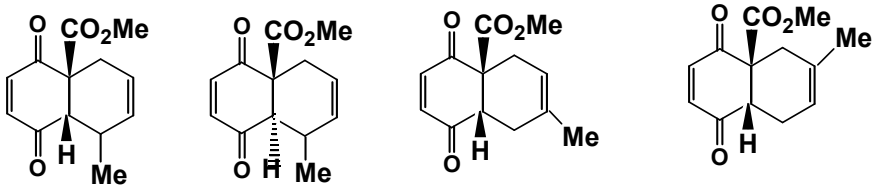
The addition of one equivalent of cyclopentadiene to 2-methoxycarbonyl-1,4-benzoquinone in methylene chloride containing a catalytic amount of TFA at -70 °C afforded a yellow-orange mobile oil which, from its ^{1}HNMR spectrum, was a 66:44 mixture of two isomers. On the basis of its ^{1}HNMR and mass spectra, the major isomer was identified as the endo-mono-adduct (XXIX). Moreover, irradiation of the mono-adduct (XXIX) in d-chloroform gave the 'box compound' (XXX) which had no resonance to low field of δ 6.22. On the basis of the ^{1}HNMR and mass spectra, the minor isomer was identified as the (XXXI). The mechanism in figure (2) is suggested. Precedents for such a rearrangement reaction have been set. 2-Acetyl-5,6-dichloro-1,4-benzoquinone cyclopentadiene mono-adduct, on pyrolysisl, gives the benzofuran derivative (XXXII). Finch[14] also quotes further examples of rearrangements of this type.[15,16] The proposed mechanism[17] is shown in figure (3) and involves carbon-carbon bond heterolysis and quenching of the resultant allylic carbocation by the adjacent carbonyl group. Coville[13]has suggested that three isomers are formed in the ratio 75:7:18, assigned as (XXIX), (XXXIII) and an endo-mono-adduct conformer (XXXIV) or (XXXV), respectively. He could only isolate the major isomer (XXIX). Isomer (XXXIII) is due to the addition of cyclopentadiene to the unsubstituted ethane linkage of the quinone, which by using TFA, i.e. increasing the electron deficiency of C-3 of the substituted ethane linkage, should be formed to a less extent.

Sublimation of the crude mono-adduct mixture at 120-125 °C/0.1 mmHg gave a pale yellow oil, the ^{1}HNMR spectrum of which showed almost pure endo-mono-adduct. The reaction was repeated at room temperature without TFA; a 76:24 mixture of endo- (XXIX) and exo-(XXXVI) mono-adducts was formed. Thermolysis of this mixture at different temperatures was tried. It was concluded that the higher the temperature, up to ca. 130 °C, the higher the proportion of the exo-isomer; thermolysis in 1,2-dichlorobenzene (b.p. 180 °C) gave a dark complex mixture, probably (NMR) mainly methyl gentisate resulting from decomposition of the adducts. Decomposition of the mono-adduct at high temperature is expected, since one of the two new σ-bonds is particularly weak. Thus the endo-adducts are kinetically favoured, and the exo-adducts are thermally favoured.

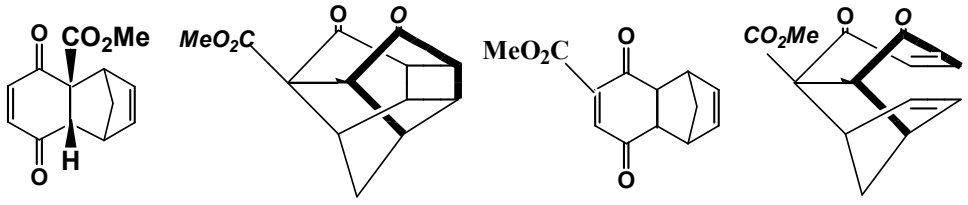
The reaction between two spiro-compounds and 2-methoxycarbonyl-1,4-benzoquinone were also carried out which resulted in a mixture of two mono-adducts with a ratio of 1:1 to 2:1 which the mono-adducts could not be separated, but on irradiation were converted to an interesting cage compound (XXXVII).



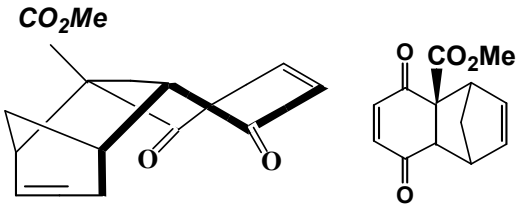
XXI *XXII* *XXIII* *XXIV*



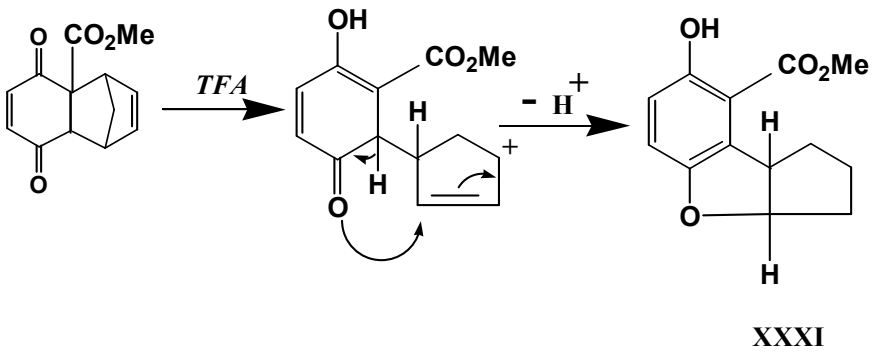
XXV *XXVI* *XXVII* *XXVIII*



XXIX *XXX* *XXXIII* *XXXIV*



XXXV *XXXVI*



XXXI

Figure 2

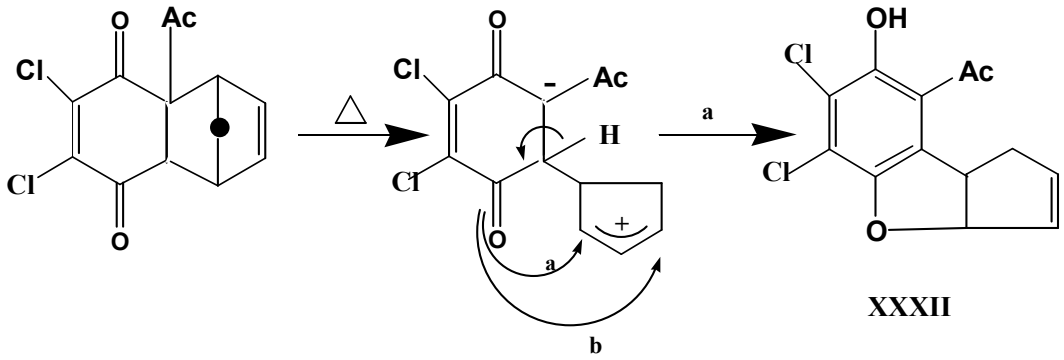


Figure 3

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